MORPHOLOGICAL AND ELEMENTAL ANALYSIS OF FINE PARTICULATE MATTER ($PM_{2.5}$) AT BACKGROUND STATION IN MALAYSIA

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by

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LIST OF ABBREVIATIONS

°C	Degree Celsius
$\mu g/m^3$	Microgram per Cubic Meter
µm	Micrometer
Al	Aluminium
ANOVA	Analysis of Variance
API	Air Pollutant Index
As	Arsenic
Ba	Barium
BC	British Columbia
Bi	Bismuth
Ca	Calcium
Cd	Cadmium
CH_4	Methane
Cu	Copper
DMRT	Duncan’s Multiple Range Test
DOE	Department of Environment
E.	East

E-BAM	Environmental Beta Attenuation Monitor
EDX	Energy Dispersive X-ray Spectrometer
E.S.E.	East-southeast
F	Fluorine
Fe	Iron
FESEM	Field Emission Scanning Electron Microscopy
IT – 1	Interim Target 1
IT – 2	Interim Target 2
K	Potassium
km	Kilometer
m/s	Meter per Second
Mg	Magnesium
Mn	Manganese
Na	Sodium
N.E.	Northeast
Ni	Nickel
NmHC	Non-methane Hydrocarbon
N.N.W	North-northwest
NO_2	Nitrogen Dioxide

NO_x	Nitrogen Oxides
O_2	Oxygen
O_3	Ozone
Pb	Lead
PM	Particulate Matter
PM_{10}	Particulate Matter with Aerodynamic Diameter Less Than 10 µm
$PM_{2.5}$	Particulate Matter with Aerodynamic Diameter Less Than 2.5 µm
Rb	Rubidium
S	Sulphur
S.	South
Se	Selenium
S.E.	Southeast
SEM	Scanning Electron Microscopy
Si	Silicone
SiO_2	Silica
SO_2	Sulphur Dioxide
SPSS	Statistical Packages for Social Sciences
S.S.E.	South-southeast
THC	Total Hydrocarbon

U.S. EPA	United States Environmental Protection Agency
UKM	Universiti Kebangsaan Malaysia
UV_b	Ultraviolet B
V	Vanadium
W.	West
WHO	World Health Organization
Zn	Zinc

ANALISA MORFOLOGI DAN KEUNSURAN BAGI PARTIKEL HALUS TERAMPAI ($PM_{2.5}$) DI STESEN RUJUKAN MALAYSIA

ABSTRAK

Pengawasan dan pensampelan kepekatan $PM_{2.5}$ telah dijalankan di stesen rujukan Malaysia (Jerantut). Tujuan kajian dijalankan adalah untuk menghuraikan morfologi dan komponen unsur bagi $PM_{2.5}$ bermula dari mengenal pasti sumber munasabah, memperincikan kepekatan $PM_{2.5}$ dan mengkaji sumber munasabah bagi $PM_{2.5}$ berdasarkan unsur-unsur yang telah dikenalpasti. Sumber-sumber munasabah dikenalpasti melalui profil tapak dalam radius 10 km dari stesen pengawasan. Hasil dikenalpasti melalui profil tapak, kebanyakan sumber munasabah datang dari arah tenggara dan dibahagikan kepada tiga kumpulan iaitu, sumber dari kilang, tapak pembinaan dan lalulintas dari Bandar Jerantut. Kemudian, statistik perihalan, plot kotak, variasi diurnal dan korelasi Pearson dibina menggunakan perisisan *Statistical Packages for Social Sciences* (SPSS) dalam memperincikan kepekatan $PM_{2.5}$. Kepekatan $PM_{2.5}$ berada dalam julat 6 $\mu g/m^3$dan 98 $\mu g/m^3$ dan purata kepekatan adalah 33 ± 16 $\mu g/m^3$, di mana ianya melepasi garis panduan *World Health Organization* (WHO). *Field Emission Scanning Electron Microscopy with Energy Dispersive X-ray Spectrometer* (FESEM-EDX) digunakan untuk menganalisa morfologi dan komponen unsur bagi setiap partikel dan partikel kemudiannya diklasifikasikan mengikut sumber. Sumber-sumber yang telah dikenalpasti adalah sumber antropogen, semulajadi dan biologi. Partikel dari sumber antropogen dan

semulajadi dikenalpasti berdasarkan morfologi dan komponen unsur mereka, sementara partikel biologi dikenalpasti berdasarkan morfologinya sahaja. *Analysis of Variance* (ANOVA) sehala dan ujian pelbagai julat Duncan digunakan untuk analisis selanjutnya ke atas unsur-unsur dari partikel antropogen dan sumber-sumber munasabah bagi partikel antropogen adalah daripada kilang, tapak pembinaan dan lalulintas. Sumber-sumber yang terdapat di stesen rujukan, majoritinya adalah daripada sumber biologi. Walaubagaimanapun, sumber-sumber yang lain juga member kesan terhadap penghasilan $PM_{2.5}$ iaitu sumber dari kilang-kilang, tapak pembinaan, lalulintas dan sumber semulajadi.

MORPHOLOGICAL AND ELEMENTAL ANALYSIS OF FINE PARTICULATE MATTER ($PM_{2.5}$) AT BACKGROUND STATION IN MALAYSIA

ABSTRACT

Monitoring and sampling of $PM_{2.5}$ concentrations were held at background station of Malaysia (Jerantut). The aim of this research is to analyze the morphological and elemental compositions of $PM_{2.5}$ then identifying the sources of $PM_{2.5}$. Potential sources were identified by site profiling within 10 km radius from the monitoring station. Then statistical analysis and Pearson correlation were conducted using Statistical Packages for Social Sciences (SPSS) program in describing $PM_{2.5}$ concentration. Field Emission Scanning Electron Microscopy together with Energy Dispersive X-ray Spectrometer (FESEM-EDX) were used to analyze morphological and elemental compositions of each particle and the particles were classified based on the major sources; anthropogenic, natural and biological. The abundant of potential sources came from southeast direction and were classified into three groups; industries, constructions and traffic from Jerantut town. $PM_{2.5}$ concentration was in the range of 6 $\mu g/m^3$ to 98 $\mu g/m^3$ and the average was 33 ± 16 $\mu g/m^3$which exceeded the World Health Organization (WHO) guidelines. The most abundant particles found in Jerantut were biological particles with 52%, followed by anthropogenic particles (45%) and natural particles (3%). The major elements in anthropogenic particles were Na and Ba, while for natural particles were S and K. One-way Analysis of Variance (ANOVA) together with Duncan's Multiple Range

Test were used for further classification of elements from the anthropogenic particles and the sources identified were industrial, construction and traffic. Therefore, based on the morphological and elemental analysis of $PM_{2.5}$ in Jerantut, majority of the sources of $PM_{2.5}$ at the background station came from biological sources, but industrial, constructions, traffic and natural sources also contributed significantly to $PM_{2.5}$ emissions.

CHAPTER ONE

INTRODUCTION

1.1 Background

Existence of impurities or pollutant substances in the atmosphere that obstruct human health or produce other adverse environmental effects are called air pollution (USEPA, 2015). Impurities also affect structures and other engineered systems, such as the impurities in rainfall (e.g. nitrates and sulphates) that render it more corrosive than would be expected (i.e. acid rain). Therefore, the characteristics of the pollutant and the origin of the chemical need to be considered.

The atmosphere is not only a dry mixture of permanent gases, but it also has other compositions that vapour from both water and organic liquids and particulate matter (PM) that held in suspension. The United States Clean Air Act of 1970 established the National Ambient Air Quality Standards to address six air pollutants that are particulate matter (PM), carbon monoxide (CO), ozone (O_3), nitrogen dioxide (NO_2), sulphur dioxide (SO_2) and lead (Pb).

Particulate matter (PM) is a complex mixture of liquid droplets and small particles which can be divided into fine and coarse particulate matter, where aerodynamic size of fine particulate is less than or equal to 2.5 μm but greater than 1 μm and aerodynamic size of coarse particulate is less than or equal to 10 μm but greater than 2.5 μm (USEPA, 2015). Their effect on public health and their activity in heterogeneous chemistry have been well known (Dockery and Pope, 1994; Höller et al., 2002). In perforating through the respiratory passageways and more damaging when entered lung tissue, smaller particles were proven to be more efficient. This is because of the participation in the atmospheric chemistry are increasing due to the increment of surface area, but inversely proportional with individual particle diameter (Neer & Koylu, 2006).

A complex mixture of elemental and organic carbon, ammonium, nitrates, mineral dust, sulphates and traces of elements is called atmospheric particulate matter. Based on gaseous precursor, atmospheric PM may be formed in the atmosphere or it may be directly discharged into the atmosphere from both anthropogenic (human activity) and natural sources (Aldabe et al., 2011). Besides vehicular traffic and smelting industries, other sources of air pollution are from coal-fired power plant, natural soil, road fugitive dust (Zhou et al., 2014), crustal sources, and vehicle exhaust where it may comprise of oil combustion or diesel engine exhaust sources (Hieu and Lee, 2010). In Malaysia, the major sources of air pollution are motor vehicle, power plants, industries and open burning (DOE, 2012).

In recent years, morphological and elemental properties of individual ambient air particle are getting significant attention regarding their effect on radiative and elemental characterization. Besides that, information about their source, ambient air history, transport, reactivity, formation and removal of ambient air can be received from a detailed properties of individual ambient air particle (Lu et al., 2006; Adachi and Buseck, 2010; Lee and Hieu, 2013; Pipal and Satsangi, 2015). For example, PM_{10} that contain peculiar elements, such as Ca, Fe, K, Si, Mg and Na are presumably come from the soil, but elements and organic carbon, which probably come from combustion sources are contained in finer particles (Xie et al., 2005; Schwarz et al., 2008).

$PM_{2.5}$ (particulate matter with aerodynamic diameter less than or equal to 2.5 μm) has found to be more harmful to human health than larger particles (Kappos et al., 2004), so attention has shifted to the investigation of ambient $PM_{2.5}$. $PM_{2.5}$ of a site can be monitored and sampled by using E-BAM, E-Sampler, High Volume Sampler and other air quality control equipments. From the monitoring, the average $PM_{2.5}$ concentration can be determined. Some of the equipments were equipped with meteorological sensors, ambient temperature, wind speed, wind direction and relative humidity, and the correlation between $PM_{2.5}$ and meteorological parameters can also be calculated.

Pöschl (2005) indicated that particle size, chemical composition and mixing states of atmospheric aerosols pose a significant impact on human health. Therefore, it is essential to understand physical and chemical characteristics of $PM_{2.5}$. Scanning electron microscopy with energy-dispersed X-ray analysis (SEM/EDX) is commonly used for a single particle study (Shi et al., 2003; Li et al 2010b). It provides useful information on the morphology, elemental composition and particle density of aerosols and also gives a better insight about the source of particles (Conner and Williams, 2004; Bernabe et al., 2005; Cong et al., 2010). In order to improve the air quality, efforts must be made to understand the physical and chemical characterization of airborne $PM_{2.5}$ and to identify the potential sources.

1.2 Problem Statement

Airborne particulate matter (PM) and its public health impact is proven in revealing harmful health effects at exposures experienced by urban populations (Pope and Dockery, 2006; WHO, 2005). Hence, extensive researches on airborne particulate matter are required for the policy on air quality and protection on human including the environment. Knowledge, especially on particulate matter's origin, identification on particles that may be hazardous to the quality of life, including the environment is necessary to improve the impacts on human and natural ecosystem (Hellebust et al., 2010).

Jerantut was established by Department of Environment, Malaysia (DOE) as the background station to monitor the general background concentrations of selected air pollutants in the Peninsular Malaysia (Latif et al., 2014; Fritz et al., 2015). Latif et al. (2014) studied a fifteen-year data of air quality at Jerantut. From the study, PM_{10} concentration has elevated in the study area due to the increment of several sources. As PM_{10} concentration has elevated, $PM_{2.5}$ concentration may also increase. Therefore, as a consequence of increasing number of sources that lead to increment of $PM_{2.5}$ concentration, various types of morphological characteristics and elemental compositions of $PM_{2.5}$ are expected. Air pollution studies in Malaysia rather focus on PM_{10} which has an aerodynamic diameter less than 10 micrometers. However, morphological and elemental characteristics of particulate matter with aerodynamic diameter equal to or less than 2.5 micrometers are not frequently studied in Malaysia. Hence, the data of morphological and elemental of $PM_{2.5}$ are inadequate.

Therefore, this research was conducted to identify the morphology of $PM_{2.5}$ and to determine the elemental compositions of $PM_{2.5}$ emitted from sources in background station of Malaysia. Sources of $PM_{2.5}$ were investigated from site profiling nearby to the monitoring station.

1.3 Research Gap

In Malaysia, $PM_{2.5}$ is not widely monitored and many past researches that have been conducted in Malaysia rather focusing on PM_{10} and other pollutants. Studies on $PM_{2.5}$ have been carried out by Amil et al. (2015), Ee-Ling et al. (2015), Fujii et al. (2015), Khan et al. (2015) and Khan et al. (2016), but none focused on morphological analysis. Latif et al. (2014) carried out a research on a fifteen-year dataset focusing on ten major air pollutants that consisted of CO, NO, NO_2, NO_x, SO_2, PM_{10}, ground level ozone (O_3), methane (CH_4), total hydrocarbon (THC) and non-methane hydrocarbon (NmHC) while four meteorological variables consisted of wind speed, ambient temperature, relative humidity and ultraviolet-B radiation (UV_b) from the background station. Awang et al. (2013) evaluated the trend and status of ozone concentration in Malaysia for 2009 at Kajang (urban), Seberang Perai (industrial), Bakar Arang (sub-urban) and Jerantut (background station), while Banan et al. (2013) identified and described the variations in O_3 concentrations recorded from 2005-2009 at Petaling Jaya (urban), Putrajaya (sub-urban) and Jerantut (rural). The trend and status of five air pollutants (CO, NO_2, O_3, PM_{10} and SO_2) and their correlations with the meteorological factors were determined at different air monitoring stations in Klang Valley by Azmi et al. (2010). While Amil et al. (2014)

identified the mass concentrations of $PM_{2.5}$ and its relation to elemental compositions and related gaseous-meteorological parameters during 2011 haze episode at UKM Bangi, this study described the level of $PM_{2.5}$ concentration and meteorological parameters, analyzed the morphological and elemental characteristics and investigated the possible sources of $PM_{2.5}$ at the background station.

1.4 Objectives

The objectives of this research are:

i. To identify potential sources of $PM_{2.5}$from site profiling at background station.
ii. To analyze morphological and elemental compositions of $PM_{2.5}$.
iii. To investigate possible sources of $PM_{2.5}$ based on elemental composition analysis.

1.5 Scope of Studies

Monitoring of $PM_{2.5}$ was conducted at the background station, which is located at Stesen Meteorologi Batu Embun, Jerantut, Pahang. The monitoring was conducted for 17 days from 11^{th} of June 2015 until 27^{th} of June 2015 to identify the concentration and possible sources of $PM_{2.5}$ at the station. The 17 days of monitoring session was held to collect the information of the concentration trend for 24 hours continuously.